



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/AU91/00106 <b>(22) International Filing Date:</b> 21 March 1991 (21.03.91)  <b>(30) Priority data:</b> 233031 21 March 1990 (21.03.90) NZ 234494 13 July 1990 (13.07.90) NZ 236064 13 November 1990 (13.11.90) NZ  <b>(71) Applicant (for all designated States except US):</b> PORTWALL PTY LIMITED [AU/AU]; 77 Main Street, 1st Floor, Blacktown, NSW 2148 (AU). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> McLACHLAN, Corran, Norman, Stuart [NZ/NZ]; 29 Summer Street, Devonport, Auckland (NZ). KERKIN, Gary, Norris [GB/NZ]; 428 Thames Street, Morrinsville (NZ). VINES, Peter [NZ/NZ]; 16 Turnbull Crescent, Morrinsville (NZ).	<b>(74) Agent:</b> SMITH SHELSTON BEADLE; 207 Riversdale Road, Hawthorn, VIC 3122 (AU).  <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LIPID EXTRACTION AND PROCESSING AND PRODUCTS SO OBTAINED	
<b>(57) Abstract</b>  <p>There is described a process for separating substantially all the lipids from an aqueous liquid containing lipids comprising contacting the liquid with a subcritical or supercritical fluid at a suitable temperature and pressure and of a type such that at least part of the lipid is more soluble therein than the remaining components of the liquid, under conditions such that some of the lipids in the liquid are taken up by the fluid and then recovering such lipid from that fluid. The process can for example be used to make butter by extracting butter fat from cream using supercritical carbon dioxide.</p>	

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## LIPID EXTRACTION AND PROCESSING AND PRODUCTS SO OBTAINED

This invention relates to the recovery of lipids from a lipid containing mixture, the processing, where necessary, of the so extracted lipids and the products so obtained. In particular, the invention relates to a process for making butter.

Butter is a water-in-oil emulsion containing about 80 percent milk-fat and a maximum of sixteen percent water. Milk-fat consists of a complex mixture of fatty acids and triglycerides with carbon numbers ranging from 4 to 56. In addition it contains many minor components, the major of which are cholesterol, mono- and di-glycerides and phospholipids. Their relative composition varies from animal to animal, seasonally, and on nutrient quality and type. In addition milk-fat contains vitamins A, D and carotene.

The combination of delicate flavours and broad range of melting point gives rise to a unique product which has proved impossible to duplicate using other liquids such as vegetable oils. However, in recent years concern over the presence of cholesterol and saturated fats in milk-fat has led to rising consumer resistance to its traditional use, due to their identification with heart disease.

This invention is broadly concerned with a process for separating lipids from a lipid containing mixture which in the case of butter making removes the need for a churning step and optionally allows cholesterol to be removed, whilst still allowing the production of milk-fat at economical costs.

Continuous manufacture of butter is fully described in **International Dairy Federation Bulletin**, No. 204, 1986. It sets out the following features as major influences on the quality of butter:

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**Cream storage:**

Quality requirements necessitate heating to 50-70°C for short times followed by cooling to 5°C.

**Organoleptic quality:**

Elimination of off-flavour due to animal feed or improper handling may be required.

**Fat content:**

The fat content of the cream influences fat loss on churning.

**Acidity, pH:**

These also influence fat loss on churning.

**Chemical composition of the fat:**

Affects melting and spreading properties of butter.

**Microbiological:**

Presence of bacteria affects product taste and storage properties.

**Fat breakdown:**

Occurs as a result of either hydrolysis or oxidation. Hydrolysis may be catalysed by natural milk lipases or introduced bacterial lipases.

The process of the invention is designed to achieve a good balance of the most desirable of these features.

Continuous butter-making processes documented in IDF Bulletin No. 204 include Fritz, Alfa, Alfa-Laval, New Way, Meleshin, Cherry Burrell and Creamery Package.

With the exception of the Russian Meleshin process, the most commonly used process is the Fritz which most nearly duplicates traditional batch churning.

The process consists of a large variable speed churning cylinder, a big separating cylinder for separating the butter milk from the butter grains, a low-speed working section, a vacuum chamber and a second working chamber.

Fat losses occur during the separation of the buttermilk which may contain a residual fat content of 3-10gm/l. This corresponds to 0.5-1.5 percent of the butter-fat leaving the plant. In addition approximately 40 percent of the phospholipids are lost in the buttermilk.

As well as the process described above, a process involving carbon dioxide addition during butter-making, called the Senn process, has been described in the literature: French Patents 764,584 and 865,787 (1947). Very rapid production of butter was claimed with the presence of the carbon dioxide assisting coagulation of the fat-in-water emulsion. Despite its claimed advantages, this process does not seem to have been commercialised.

Supercritical fluids are found to be useful in removing undesirable components from food products or extracting desired material from a range of plant and animal materials.

The use of supercritical carbon dioxide in particular to remove caffeine from coffee beans, either roast or green, or aqueous coffee extraction is well documented:

Canadian Patent 1,132,836. Zosel, K, (1982); US Patent 4,749,622, Kamerei, (June 1988); US Patent 4,692,280, Spinelli et al, (September 1982).

In addition, patents have been filed covering the removal of cholesterol from substances such as butter and described in the literature "Modifications of butter oil by extraction with

Supercritical carbon dioxide". Agric. Biol. Chem. 50 (5,1987) 1709-1715, Japanese Patent No. 134042 (1987). Shishikura et al.

A more economical process has been described in our patent, NZ Patent Application 221503 (1987). This patent is a general one covering the removal of cholesterol from lipids with extraction from anhydrous milk-fat being a particular example.

In accordance with this invention there is provided a process for separating substantially all the lipids from a lipid-water mixture comprising bringing a subcritical or supercritical fluid at a suitable temperature and pressure and of a type such that at least part of the lipid is more soluble therein than water, into contact with the mixture, in an extractor under conditions so that at least part of the lipid component in the mixture is taken up by the fluid and then recovering the lipid from that fluid.

The invention is particularly concerned with the production of butter or butter-fat fractions. The starting material for normal butter production, namely cream, is an oil in water emulsion. The invention will be described with reference to the production of butter from cream, but it is not to be considered as limited thereto. Concentrates prepared by removal of water from whole-milk according to the known art, may be used.

In the process of this invention cream is separated from milk by centrifugation, according to the known art. Alternatively the volume of milk is reduced by a prior concentration step in which water is removed by reverse osmosis or evaporation or the like. The concentration of milk-fat in the cream can be preferably anywhere from 10-80 percent and more preferably 20-50 percent.

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The concentration of milk-fat in the liquor to be subsequently extracted is not crucial to the success of the process but is largely determined from economic consideration regarding the size of the high pressure extraction equipment. Too high concentration of milk-fat in the cream may give rise, however, to unnecessary fat losses in the course of separation.

During this separation the temperature of the cream may be raised to 50-80°C, preferably 50-60°C, to ensure that a substantial reduction occurs in the risk of lypolysis due to the natural lipases, or introduced lipases, in the milk. Temperatures above 60°C are generally undesirable due to the possible damage to heat sensitive proteins in the milk.

The cream may then be passed through a degassing chamber to ensure that air or other gases are removed. Degassing may take place under vacuum and optionally with the injection of live steam at low temperature, or it may be effected by any process known to the art which is suitable and which does not raise the temperature of the cream above the limits described above. It is then fed directly to the carbon dioxide extraction apparatus or may be cooled to 5°C-10°C for storage.

The cream is then heated or cooled, as the case may be, to the temperature of the extraction system by passing it through a heat exchanger, as known to the art, from which it is fed to the extraction column.

When cream is treated with carbon dioxide at a high pressure, the amount of the lipid fraction that is extracted into the carbon dioxide fluid varies with the temperature of the extraction. When the carbon dioxide is in a supercritical state, substantially all of the lipid materials will be extracted into the supercritical fluid. When the temperature is below the critical temperature fractionation of the lipids

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may occur as described in our NZ Patent Application, 236,285 (1990) and copending PCT application filed simultaneously herewith. The methods described in that specification may be incorporated in the processes of this invention.

Under supercritical conditions, the pressure and temperature conditions can be chosen so that the water solubility in carbon dioxide is maximised whilst lipases are completely or partially inactivated. The differential density between the supercritical fluid and water can also be maximised within the above constraints to facilitate separation of any non-lipid components in the cream not dissolved.

The fluid is preferably carbon dioxide but  $N_2O$ ,  $SF_6$ ,  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CH_2CF_2$ ,  $C_3F_8$ ,  $CHF_3$ , ethane, propane, butane, ethylene or acetone, which are considered unobjectionable from a health point of view can also be used. Mixtures of these fluids can be used. This invention will be further described with reference to the use of carbon dioxide alone.

The high pressure carbon dioxide that is used in the extraction column may be used alone or may contain an amount of water up to the amount which will saturate it under the particular conditions of temperature and pressure used in the extraction process. It is generally saturated when re-cycled in accordance with the process of this invention.

The conditions of temperature and pressure under which the extraction is effected may vary for reasons mentioned above depending upon the desired product. The temperature at a minimum will be sufficient under the conditions of pressure employed to achieve sufficient dissolution of a desired fraction of the lipids. This will normally be above  $0^\circ C$ . The maximum temperatures will be mainly determined by cost constraints and the desire to avoid damage to heat sensitive ingredients in the butter-fat or other desired product. The temperature will thus be between  $0^\circ C$  and  $80^\circ C$ . Where a



fractionation of the lipids is desired, the temperature will preferably be between  $-10^{\circ}\text{C}$  and  $31^{\circ}\text{C}$ , more preferably  $0^{\circ}\text{C}$  to  $31^{\circ}\text{C}$  as described in our application No. 236,285. If total removal of the lipids is desired, the temperature will preferably be between  $30^{\circ}\text{C}$  and  $80^{\circ}\text{C}$ , more preferably between  $40^{\circ}\text{C}$  and  $60^{\circ}\text{C}$ . The pressure is generally between 75 bar and 350 bar and more preferably between 150 bar and 280 bar. The minimum pressure will be dictated by the need to achieve a satisfactory dissolution of the desired lipid fraction(s) in the carbon dioxide stream.

Water has a relatively limited solubility in sub- or supercritical carbon dioxide which increases with temperature at constant pressure whereas carbon dioxide solubility for lipids decreases with temperature at constant pressure.

To achieve the optimum separation of the lipids from the liquor the carbon dioxide should intimately contact the surface of a thin film of the fat-in-water emulsion in a continuous co-current or counter-current manner. The emulsion may be converted into the form of a thin film in any known manner as, for example, by passing the fat-in-water emulsion over a surface in the form of a thin film covering the same; by passing the emulsion through a cascade or packed bed, containing rings or other distribution systems known to the art, or a device which corresponds to a thin film surface evaporator or the like, or by spray nozzle or other droplet generating device. Alternatively the extraction may take place in a liquid-fluid extraction involving plate mixer-settler units. It is not intended that the separation process be limited but is to follow process steps well recognised in the art of chemical engineers.

In some instances it may be preferable to add an additional water stream to the extractor so that the upper section of the column contains high pressure solvent in contact with fresh

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water which acts as a scrubbing section. The purpose of this "washing or scrubbing" is to remove any particulate matter entrained in the high pressure fluid and to extract any undesirable components extracted from the buttermilk with the fat that are preferentially soluble in water. In some instances this water may be replaced by dilute milk-of-lime suspension or dilute sodium hydroxide solution, or any suitable alkaline solution.

The amount of carbon dioxide will be sufficient to dissolve the milk-fat and hence will be preferably 30-150 times the weight of milk-fat to be dissolved.

At 200 bar and 50°C the solubility of water in supercritical carbon dioxide is about 0.3 w/w percent - Wiebe R & Gaddy V L, J. Am. Chem. Soc. 63,475 (1941) - whereas at 50°C and 75 bar it is 0.142 w/w percent and at 31°C and 75 bar it is about 0.09 w/w percent.

At 200 bar and 50°C a recirculation ratio of about 80:1 (carbon dioxide: water) on a weight/weight basis is required. Under these conditions the ratio of fat to water in the carbon dioxide is between 2:1 and 10:1.

An important feature of the invention is to then reduce the cholesterol content in the lipid fraction in the high pressure fluid stream to produce a low-cholesterol product, preferably a cholesterol-free product. The cholesterol can be removed by methods known in the art, such as using an adsorbent. The adsorbent can be an inorganic compound or organic compound, which preferentially adsorbs cholesterol. There are many such adsorbents described in the literature. It is preferred within the scope of this invention, to use an adsorbent which selectively removes cholesterol and thus leaves behind a cholesterol free product and at the same time removes only a small amount if any, of the lipid. The preferred materials are

those described in our NZ Patent Application No. 221503 (PCT Appln No. GB 88/00739). The processes for adsorbing cholesterol from a lipid-laden high-pressure carbon dioxide stream as discussed in that specification are also methods which can be used in this invention.

The invention also provides a method whereby the adsorbent step can take place during the washing step. Thus, for example, if milk of lime is used in the washing step in the column, then calcium carbonate is formed during that process which is the most preferred adsorbent for use in this invention. The calcium carbonate will precipitate and take with it cholesterol. The amount of milk of lime added to the stream of high pressure carbon dioxide/lipid has to be calculated accurately in order to ensure that the solvent characteristics of the high pressure carbon dioxide for the lipid in the cream is not changed to such an extent that the lipid itself begins to precipitate out.

Cholesterol may be recovered from the adsorbent by any method known to the art and preferably by eluting it with a solvent which may be a subcritical or supercritical fluid optionally with the addition of a cosolvent. Such elution may take place in situ or otherwise.

The cholesterol-free or low-cholesterol product is then passed through depressurisation and heating cycles to recover it from the fluid. The dissolved material may be recovered when the fluid is in the supercritical state through an increase in temperature at constant pressure or by lowering the temperature and pressure but remaining supercritical or alternatively by reducing the temperature and pressure to subcritical conditions. When the fluid is in a subcritical state the product can be recovered by reducing the pressure and/or increasing the temperature. The dissolved material may be recovered as a mixture of water and lipids or alternatively as

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two separate phases, namely a fat-free aqueous phase and an essentially anhydrous lipid phase.

The recovered mixture of milk-fat, vitamins, water and phospholipids is then suitably degassed at 30-80°C, preferably 30-40°C, and subsequently cooled to 15-20°C by pumping it through a degassing chamber in which carbon dioxide and any residual off odours are removed. Degassing may be effected by vacuum, or by nitrogen sparging into a vacuum or low pressure, or by any method known to the art.

The degassed milk-fat and water mixture is then fed to a wiped film heat exchanger or other device where it is worked to allow crystal growth and the production of butter according to the known art in butter or edible fat manufacture so as to prepare a product of the desired physical properties. If required and preferably if it has been produced by fractionation as cited above, the degassed butter may be blended with other lipid fractions from that process to produce spreads with desired softening points, spreadability and other properties.

An important benefit of the invention is the fact that high pressure carbon dioxide is a highly effective bactericide, particularly when moist. Therefore it is possible in accordance with the invention to obtain sterile butter without the need for other micro-organism control methods such as pasteurisation or vacreation. As described above, however, it may be desirable to apply some form of degassing and heating to eliminate off-odour and inactivate lipases.

The invention has as its principal advantage the elimination of the butter churning step which in a normal butter operation causes fat losses. In the process of the invention, these losses can be reduced considerably and by suitable choice of processing conditions, eliminated almost completely.

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The attached drawing shows in schematic form the full process of the invention. Each stage of the process is identified by a numeral.

In step 1, cream is separated by a normal technique from whole milk; skim milk is the other product.

In step 2, contact between the cream and high pressure carbon dioxide occurs. Cream is fed into the top of the column, extraction vessel 1, with high pressure carbon dioxide being fed countercurrent through the bottom. The lipid/water/carbon dioxide stream is then fed to step 4, while the residue, namely water, solids-not-fat and undissolved lipids, is fed to step 3 where further separation of milk solids may be effected.

In step 4, the lipid/water/carbon dioxide stream, still under high pressure conditions, is fed to the adsorbent columns. Preferably three of these are operating in parallel, so that at any one stage one can be on stand-by, another one is being used as the adsorbent while the third is being replenished by passage of a solvent therethrough. The conditions of this process are more particularly described in our NZ Patent Application No. 221,503.

After the adsorbent, the carbon dioxide/water/lipid stream is subject to depressurisation so that the fat and water condenses in a condenser in step 6, while the carbon dioxide is fed back through step 7 (to change the temperature of the carbon dioxide to the appropriate value) and then through pump 8 to pressurise it to a suitable state.

The fat and water from step 6 are passed to a degasser in step 9, from which the carbon dioxide is returned to the recompression stage while the fat and water mix is fed to step 10 and 11 to form cholesterol-free butter. It is at this stage that lipid fractions obtained by fractionation as mentioned

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previously can be incorporated in various proportions to produce butter having a desired softening point and other desirable properties.

Alternatively step 6 may be operated so that an aqueous phase and a lipid phase coexist in the condenser. These phases may be recovered separately, the lipid phase being essentially anhydrous milk fat.

The cholesterol from step 4 is eluted from the adsorbent by carbon dioxide and recovered after depressurisation. The carbon dioxide is compressed and recycled. A cosolvent may be added.

Thus in accordance with this invention there is provided a process for making butter which has a number of advantages over existing processes.

While in the specification reference has been made to preferred embodiments, the invention is not to be construed as being limited thereto. Moreover where reference is made to a specific feature or process step and equivalents are known to exist to such feature or step, such equivalent features or steps are incorporated herein as if specifically set forth.

#### Example

Cream containing 54% moisture, 41.6% fat, 4.4% solids-not-fat, all by weight, was introduced into supercritical carbon dioxide at a rate of 1.5 kg/h. The carbon dioxide flow rate was 100 kg/h. The two fluids were contacted at a temperature of 41°C, and a pressure of 250 bar. After contact the fat-rich carbon dioxide stream was passed to a separator where dissolved fat and water were removed. The carbon dioxide was recirculated.

The material recovered from the carbon dioxide was found to contain 81.4% fat, 18.4% moisture and 0.2% solids-not-fat. Two

separate phases existed in the ratio of 82% fat-rich, and 18% aqueous. The fat-rich phase contained less than 1% moisture, and the aqueous phase contained 1% total solids (0.16% fat, 0.84% solids-not-fat).

The residue not dissolved in the carbon dioxide was recovered and found to contain 90.2% moisture. 1.4% fat and 8.4% solids-not-fat.

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WHAT WE CLAIM IS:

1. A process for separating substantially all the lipids from an aqueous liquid containing lipids comprising contacting the liquid with a subcritical or supercritical fluid at a suitable temperature and pressure and of a type such that at least part of the lipid is more soluble therein than the remaining components of the liquid, under conditions such that some of the lipids in the liquid are taken up by the fluid and then recovering such lipid from that fluid.
2. A process according to claim 1 in which the fluid in a subcritical or supercritical state is selected from carbon dioxide,  $N_2O$ ,  $SF_6$ ,  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CH_2CF_2$ ,  $C_3F_8$ ,  $CHF_3$ , ethane, propane, butane, ethylene or acetone and mixtures thereof.
3. A process according to claim 2 in which the fluid is carbon dioxide.
4. A process according to claims 1, 2 or 3 in which the lipid-water mixture is cream.
5. A process according to claim 4 in which the cream is prepared from bovine milk, or goat milk, or any other suitable mammalian milk.
6. A process according to any one of the preceding claims in which the lipid-laden fluid is contacted with a suitable adsorbent capable of removing cholesterol.
7. A process according to claim 6 wherein the cholesterol adsorbed onto the adsorbent is recovered by eluting the adsorbent with a solvent.
8. A process according to claim 7 wherein the solvent is a fluid in a subcritical or supercritical state optionally with the addition of a cosolvent.

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9. A process in accordance with claim 7 or 8 wherein the elution takes place in situ or otherwise.
10. A process according to claims 1 to 9 in which a lipid-water mixture is dewatered to any desired moisture content.
11. A process according to any of the preceding claims for the continuous production of butter and/or other milk-fat products which comprises separating the lipid components and cholesterol from cream by supercritical or subcritical fluid extraction under conditions of temperature and pressure such that solids-not-fat are freely separated, the process being carried out at a temperature between 0°C and 80°C and a pressure between 75 bar and 350 bar.
12. A process according to claim 11 in which the supercritical or subcritical fluid contains carbon dioxide either alone or as a mixture with one or more compounds selected from  $N_2O$ ,  $SF_6$ ,  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CH_2CF_2$ ,  $C_3F_8$ ,  $CHF_3$ , ethane, propane, butane, ethylene and acetone.
13. A process according to claim 12 wherein the subcritical or supercritical fluid is carbon dioxide.
14. A process according to claims 11 to 13 in which the cream contains preferably between 10% and 80% milkfat.
15. A process according to claim 14 in which the cream contains preferably between 20% and 50% milkfat.
16. A process according to claims 11 to 15 wherein the cream is prepared from milk by centrifuging, or reverse osmosis, or evaporation or any other method suited to reducing the water content of the milk.

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17. A process according to claims 11 to 16 in which the cream is treated by heating it preferably to between 50°C and 60°C and passing it through a vacuum chamber or injecting live steam or subjecting it to any other suitable method of degassing to remove off-odour and to inactivate lipases.

18. A process according to claims 11 to 17 wherein the cream is contacted with carbon dioxide under supercritical conditions at a temperature preferably between 32°C and 60°C and a pressure preferably between 200 bar and 280 bar.

19. A process according to claims 11 to 17 wherein the cream is contacted with carbon dioxide under subcritical conditions at a temperature preferably between 0°C and 30°C and a pressure preferably between 150 bar and 280 bar thus effecting a separation of lipids such that lipids of higher molecular weight remain undissolved and largely free of cholesterol.

20. A process according to claim 18 or 19 in which the temperature and pressure of the lipid-laden fluid are controlled in a step-wise manner to effect fractional recovery of the lipids.

21. A process according to claims 11 to 20 in which the lipid-laden fluid is contacted with a suitable adsorbent capable of specifically removing cholesterol.

22. A process according to claim 21 wherein the cholesterol adsorbed onto the adsorbent is recovered by eluting the adsorbent with a solvent.

23. A process according to claim 22 wherein the solvent is a fluid in a subcritical or supercritical state optionally with the addition of a cosolvent.

24. A process according to claim 21 or 22 wherein the elution takes place in situ or otherwise.

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25. A process according to claims 11 to 24 in which lipid and water are recovered from the fluid by suitable changes in temperature and pressure such that the dissolved material becomes essentially insoluble in the fluid.
26. A process according to claim 25, wherein when the fluid is in the supercritical state the material is recovered by an increase in temperature at constant pressure or by lowering the temperature and pressure but remaining supercritical or alternatively by reducing the temperature and pressure to subcritical conditions.
27. A process according to claim 25, wherein when the fluid is in a subcritical state the product is recovered by reducing the pressure and/or increasing the temperature appropriately.
28. A process according to claims 9 to 27 wherein lipid and water are recovered from the fluid as separate phases, the lipid phase being essentially anhydrous milk-fat.
29. A process according to claims 9 to 27 in which lipid and water are recovered as a mixture with appropriate compositions of butter by a suitable reduction in pressure to preferably near critical or subcritical conditions.
30. A process according to claim 29 wherein the lipid and water mixture is subsequently worked to produce butter optionally with the addition of salt.
31. A process according to claims 19 to 30 in which milk-fat and water fractions are blended in any desired combination and optionally worked to produce butters or spreads with or without the addition of salt.
32. A process according to claims 11 to 31 in which residual dissolved carbon dioxide is removed from the milk-fat by a vacuum degassing system, or a nitrogen flushing system with or without vacuum assistance, or some other suitable removal system, and preferably in which the carbon dioxide so removed is recovered.

33. A process according to claims 11 to 32 wherein the subcritical or supercritical fluid is first saturated with water.

34. A process according to claims 11 to 33 in which the cream is contacted in a thin aqueous film by passing the concentrated milk or cream downwards through a packed column or other suitable contacting device and by passing the supercritical or subcritical fluid upwards in counter-current contact therewith.

35. A process according to claims 11 to 34 wherein the cream is contacted with the subcritical or supercritical fluid in the form of fine droplets generated by injecting or spraying the cream into the fluid, or by any other droplet generating device optionally incorporating ultrasonics or radio waves or other suitable device.

36. A process according to claims 11 to 35 wherein the supercritical or subcritical fluid, after removal of the extracted materials, is recycled for further contacting with the cream.

37. A process according to claims 11 to 36 wherein one or more of the following are achieved:

pasteurisation of the cream is preferably eliminated after heating to between 50°C and 60°C to inactive lipases;

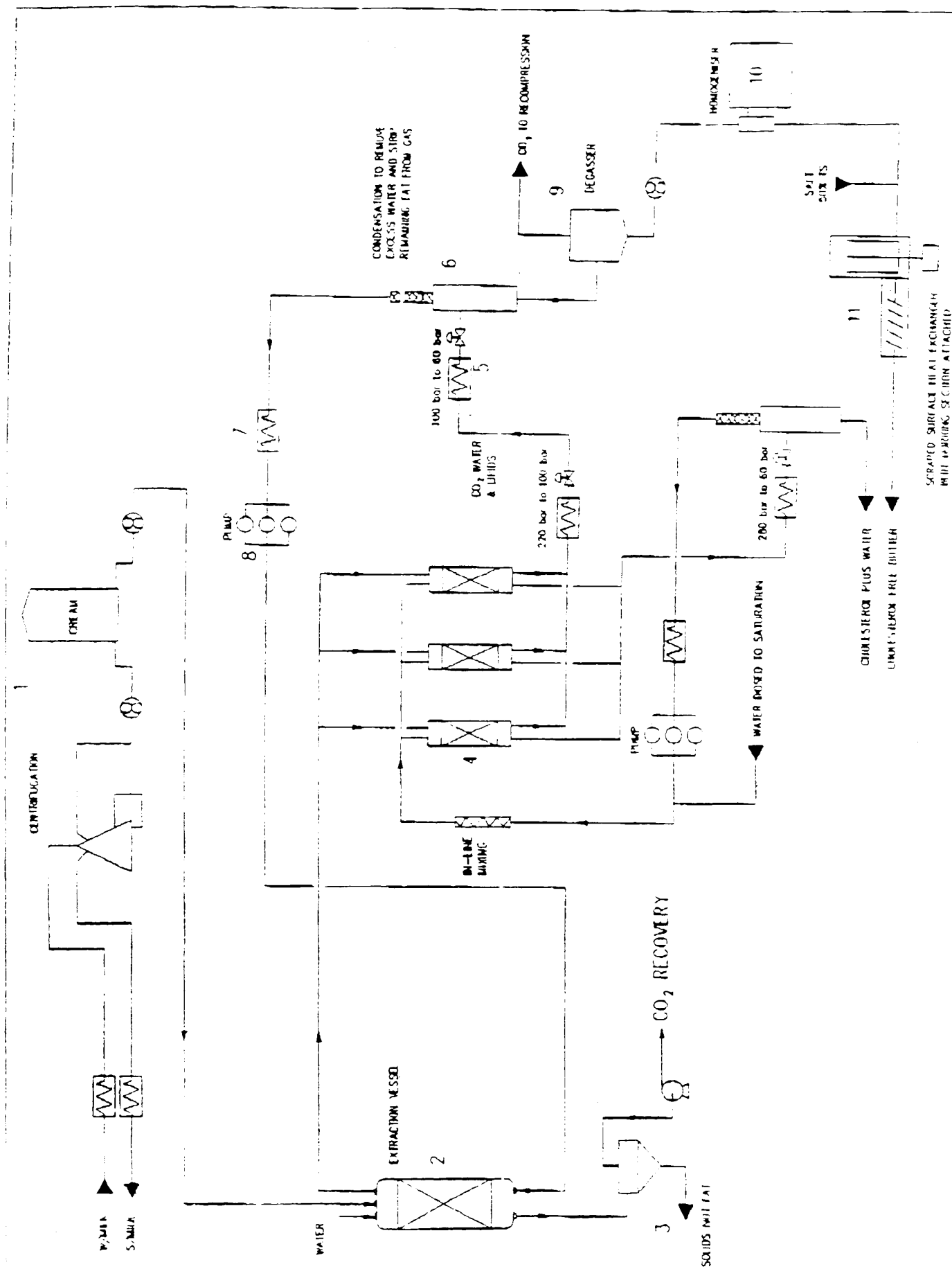
the lipid-laden supercritical or subcritical fluid is preferably washed with water, or a dilute sodium hydroxide solution or a dilute milk-of-lime suspension;

loss of fat during traditional buttermilk production is eliminated; and

the volume of milk is preferably reduced in a prior concentration step consisting of centrifugation, evaporation or reverse osmosis or other suitable concentration method.

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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 91/00106

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.<sup>5</sup> A23C 9/14, A23C 15/16

## II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
IPC	A23C 9/14, A23C 15/16, A23L 1/01, A23J 1/20

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched 8

AU : IPC as above

## III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category*	Citation of Document, with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
X,Y	US,A, 4692280 (THE UNITED STATES OF AMERICA AS REPRESENTED BY THE SECRETARY OF COMMERCE) 8 September 1987 (08.09.87) See claims	(1-37)
X,Y	CA,A, 1132836 (STUDIENGESELLSCHAFT KOHLE m.b.H. GERMANY) 5 October 1982 (05.10.82) See claims	(1-37)
X,Y	EP,A, 321055 (UNILEVER NV) 21 June 1989 (21.06.89) See claims	(1-37)
X,Y	US,A, 4504503 (LEVER BROTHERS COMPANY) 12 March 1985 (12.03.85) See claims	(1-37)

\* Special categories of cited documents: 10

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
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- \*Z\* document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search  
2 July 1991 (02.07.91)

Date of Mailing of this International Search Report

10 July 1991

International Searching Authority

Signature of Authorized Officer

Australian Patent Office

*B. Spencer* B. SPENCER

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON  
INTERNATIONAL APPLICATION NO. PCT/AU 91/00106

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members			
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END OF ANNEX